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## (54) METHOD FOR CONTINUOUS EXTRUSION MOLDING OF THERMOSETTING RESINS

(71) We, DAI NIPPON TORYO CO., LTD., a Japanese corporation, of No. 38, Nishinoshimono-cho, Konohana-ku, Osaka-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a method of forming a molded and cured product.

According to the invention, there is provided a method of forming a molded and cured product, which comprises (1) continuously extruding from an extruder through a preliminary die either into an open-ended die passage or into the space between opposed endless moving belts, an extrudable composition comprising (a) a thermosetting resin selected from unsaturated polyester resins, epoxy resins, phenolic resins, urethane resins and allyl resins, (b) a thermoplastic resin in an amount of up to 50% by weight based upon the total weight of thermoplastic resin and thermosetting resin, (c) a filler, (d) a fibrous material and (e) a curing agent, such that the extrudate from the preliminary die has a flowability corresponding to a "needle penetration degree", as defined herein, of at least 20 and such that the composition does not completely cure in the extruder or preliminary die; and (2) curing the extrudate from the preliminary die in the open-ended die passage or in the space between the opposed endless moving belts, the curing being effected at a pressure not greater than 200 kg/cm<sup>2</sup>, the average temperature of the extrudate in the die passage or in the space between the belts being from 80 to 250°C, and the residence time of the extrudate in the die passage or in the space between the belts being from 1 second to 5 minutes.

The "needle penetration degree" referred to herein is that determined under a load of 100 g for a loading time of 5 seconds according to the Test of Penetration of Butuminous Materials specified in ASTM D5.

For a better understanding of the inven-

tion, reference will now be made to the accompanying drawings in which:

Figure 1 is a flow sheet, illustrating a preferred continuous extrusion molding method in accordance with this invention;

Figure 2 is a sectional view of an example of an extrusion molding machine used for the practice of the method of this invention;

Figures 3, 4 and 5 are sectional views showing modifications of the molding machine of Figure 2;

Figure 6 is a curve showing the flow characteristics of a thermosetting phenolic resin, namely the relationship between needle penetration degree and temperature; and

Figure 7 is a curve showing the flow characteristics of a thermosetting unsaturated polyester resin, namely the relationship between needle penetration degree and temperature.

The steps of a preferred method of this invention are shown in the flow sheet of Figure 1. This method will now be described with reference to Figure 1.

At the kneading step, the components of forming an extrudable composition as used in the invention are mixed or melt kneaded to form a homogeneous composition. In order to improve the flow characteristics of the composition during extrusion molding and the quality of the resulting molded article, it is desirable that this kneading step be performed sufficiently.

In some thermosetting resins, a curing reaction occurs even at room temperature. Also, most thermosetting resins are poor in thermal stability and the range of processing temperatures is severely limited. Accordingly, the pot life of the resin and the temperature during the kneading step are very important.

The mixing of the components of the extrudable composition can be performed by various methods, and a suitable method is chosen depending on the kind of resin components. For instance, all of the components can be mixed at one time or they can be added successively. It is also possible to form in advance mixtures of some of the com-

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ponents of the extrudable composition, and finally blend them into one mixture.

The above kneading can be performed by means of, for example, a high speed disperser, a kneading roll, a hot roll, a kneader, a compression kneader, a Banbury mixer, a Henschel mixer or a screw-type extruder. The preferred kneading means depends upon the properties of the thermosetting resin used.

When a screw-type extruder is used in the kneading step, it is possible to perform the kneading and extrusion steps successively in a continuous manner. Further, the use of a screw-type extruder for kneading is advantageous in that, since the starting components are kneaded in a closed chamber, splashing or escape of the raw material can be effectively prevented. Of course, it is possible to conduct the kneading and extrusion steps separately, but when the raw material has a short pot life, it is preferable to conduct the kneading and extrusion steps in a continuous manner.

When the kneading and extrusion steps are conducted separately, the kneaded raw material is withdrawn in, for example, a liquid, massive, granular or powdery state, or in the form of a ribbon having, for example, a thickness of 2 to 3 mm, or in the form of a rope, and then it is fed to the extrusion step.

In the extrusion step, the raw material from the kneading step under atmospheric or elevated pressure may be transported by a rotation of a screw toward the end thereof. The rate of the screw rotation can be freely varied. When the extrusion step is performed by using an apparatus in which the molding material is transported along a screw provided in a cylinder, the resin is plasticized by the heating action of the cylinder and the frictional heat of the resin material *per se*, and is forwarded toward the end of the extruder.

Then, the resin material is extruded through a preliminary die. In order to keep the resin material fed to the molding step in an uncured (not completely cured) state, it is desirable to provide a heating or cooling zone in the extruder to control the degree of cooling or heating and to effect plasticization at high efficiency.

The material forwarded and compressed by rotation of the screw is pre-molded by the preliminary die and is directly extruded into an open-ended die passage or into the space between opposed endless moving belts by the feed pressure resulting from rotation of the screw of the extruder. The material extruded into the passage or into the space between the belts is cured while it is transported through the passage or through the space between the belts.

In conducting the curing step, a heating or cooling zone is provided, according to

need, in the passage or in the space between the belts for regulating the temperature during molding. For example, the inlet temperature of the passage or space between the belts can be maintained at a low level while the outlet temperature can be maintained at a high level. It is possible to maintain the entire passage or space between the belts at a constant level, or to cool the inlet of the passage or space. In this invention, it is necessary that the curing be performed at a temperature ranging from 80 to 250°C, but this is the average temperature of the extrudate in the passage or space and cooling of a part thereof is included in the scope of this invention.

The cured molded article is heated (post-cured) or cooled, if desired, to correct warp or twist, and may be cut to a desired size to obtain a final product.

The method of this invention will now be illustrated by reference to an example of a suitable continuous extrusion molding machine, namely that shown in Figure 2.

A raw material 20 comprising the components for forming an extrudable composition as used in the invention is fed to a hopper 2 of an extrusion molding machine. The raw material is gradually and successively extruded toward the end of the extruder (i.e. to the right in Figure 2) by rotation of an extrusion screw 3 mounted in a cylinder 1 while it is being kneaded. At this point the raw material is heated by friction between the resin molecules themselves and by friction between the resin component and the screw. Therefore, at this stage, a cooling medium is passed through passages 4, 5, 6 and 7 to control the temperature and the curing reaction. In the case of some raw materials, these passages can be heated by passing a heating medium through these passages.

The extrudate is then extruded through a preliminary die 11 attached to the end of the extruder by fixing bolts 13, where a desired cross-sectional configuration is given to the extruded resin material. At this stage, the curing reaction has still not occurred. At this stage, the temperature of the resin material is controlled by passing a heating medium through a passage 12 so that the resin has a viscosity corresponding to a needle penetration degree of at least 20, preferably at least 200. If the needle penetration degree is lower than 20, the flow resistance is extremely high in the preliminary die and hence, the molding material will cure due to frictional heat.

The softened material extruded from preliminary die 11 is immediately heated by a pair of semi-cylindrical molds 14 and 15 having passages 18 and 19, respectively, for a heating medium, and simultaneously compressed by cylinders 16 and 17, whereby the

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- resin is completely cured and a product 21 is obtained. In general, the extrusion is performed while the molds 14 and 15 are kept fixed, but under some conditions it is desired that molds 14 and 15 be moved at the same speed as the material extruded from the extruder. For attaining this movement, oil pressure cylinders 16, 17 and 22, 23 are provided. In such a case, cylinders 22 and 23 are used for moving molds 14 and 15 forward and backward in the extrusion direction and cylinders 16 and 17 are used for reciprocatively moving the molds in the compression direction. The cylinders 16, 17 and 22, 23 are so disposed that they can be repeatedly operated by means of a suitable control device.
- In the curing step, in order to smoothen the surface of the molded article it is necessary that the surface of the resin material be closely contacted with the mold or the resin material be compressed into the mold until the resin is sufficiently cured. More specifically, it is necessary that the curing step be performed at a temperature of 80 to 250°C, under a pressure not higher than 200 kg/cm<sup>2</sup> for a residence time of the resin in the mold ranging from 1 second to 5 minutes.
- In addition to the molding apparatus shown in Figure 2, in order to accomplish the compression and heating continuously, an apparatus such as shown in Figure 3 can be employed. In the apparatus shown in Figure 3, the kneaded material is extruded between a pair of heated endless belts 31 and 32 running from die 30. When this apparatus is used, a sheet-like article 33 can be prepared continuously.
- Also an apparatus such as shown in Figure 4 can be used for practice of the method of this invention, and in this case a hollow molded article can be prepared continuously. A tube-like, softened material is extruded from die 42 of extruder 41 into a heated open-ended die passage 43. Then, a stopper 46 is fixed to the end of the molded article 44 and compressed air 45 is blown into the hollow portion of the tube-like material to inflate it so that it is closely contacted with the surface of the passage, whereby a cured product 44 having a desired configuration can be obtained.
- Further, an apparatus such as shown in Figure 5 can be used. When this apparatus is employed, a raw material extruded from die 52 of extruder 51 is passed through an open-ended die passage 53 provided with a pressure-reducing chamber 55 and air-permeating holes 56, and the material is extruded while it is closely contacted with the surface of the passage by pressure reduction, whereby a molded article having a desired configuration can be obtained.
- In each of the foregoing embodiments, the heating to cause curing can be accomplished by, for example, hot air, far infrared radiation or induction heating.
- If desired, a post-curing step is conducted to remove the residual distortion from the molded article or to attain complete curing of the molded resin.
- It is important that withdrawal of the molded article be performed so that no unbalance is brought about between the withdrawal speed and the extrusion speed. If such unbalance is brought about, the residual distortion in the product becomes great. In view of the foregoing it is preferable that the withdrawal tension be not higher than 5 kg/cm<sup>2</sup> of the section area of the molded article.
- In the continuous extrusion molding method of this invention both the flow characteristics and curing characteristics of the molding material are very important factors. Accordingly, the physical and chemical properties of thermosetting resins to be used in this invention will now be described.
- In general, the thermosetting resins used have flow characteristics such as shown in Figures 6 and 7. More specifically, when a thermosetting resin is heated, from the vicinity of the point *a* the resin is plasticized and its needle penetration degree abruptly increased. However, if the temperature is further elevated and reaches the vicinity of the point *b*, the needle penetration degree is reduced because of the curing reaction, and at the final stage the resin is completely cured and it exhibits no flowability even under application of pressure (point *C*).
- In this invention, the raw material extruded from the die has a needle penetration degree of at least 20 (i.e. within a range of from point *A* to point *B* in the drawing).
- Accordingly, in this invention it is necessary to impart optimum flow characteristics to the resin material by adjusting the temperatures of the extruder and preliminary die so as to be within a range such that curing will not occur. Further, the flow characteristics of the resin material, i.e. the needle penetration degree, can be controlled appropriately by adjusting the mixing ratio of the components of the molding material, for example, the mixing ratio between the thermosetting resin and filler.
- The curing characteristics of a thermosetting resin depend upon the catalyst, curing agent and curing promoter, the mixing ratios of these agents, the temperature of curing, the residence time, and other factors.
- The flow characteristics of an ordinary phenolic resin are shown in Figure 6, and Figure 7 is a diagram showing the flow characteristics of the unsaturated polyester resin used in Example 3 hereinbelow.
- The method of this invention is performed in a continuous manner and hence, high manufacturing efficiency can be attained. A

variety of molded articles differing in cross-sectional configuration can be prepared merely by changing the die passage. When a screw-extruder is used, variation in the molding pressure is very small, and hence, it is possible to obtain uniform products.

The following articles are examples of those which can be obtained by the method of this invention:

- 10      (1) Products having a curved surface;
- (2) Pipes and tubes;
- (3) Extrusion-coated molded articles;
- (4) Molded articles having a complicated cross-sectional configuration;
- 15      (5) Hollow molded articles.

The thermosetting resins used in this invention are resins that can be cured either at room temperature or under heating to give cross-linked products having a three-dimensional structure. In this invention, there are used unsaturated polyester resins, phenolic resins, epoxy resins, urethane resins, or allyl resins. They may be liquid, solid, powdery or granular, or they may have a gel-like or fibrous form. These resins can be used singly, or mixtures of two or more of them can also be used. When two or more thermosetting resins are used in combination, it is necessary not to choose a combination of resins among which there is no compatibility or in which the curing reaction is extraordinary accelerated or retarded by mixing. In view of the compatibility with a filler and heat resistance, the use of an unsaturated polyester resin is especially preferred.

By the term "unsaturated polyester resin" used herein are meant condensation products between an unsaturated polybasic acid (or anhydride thereof), or its mixture with a saturated polybasic acid (or anhydride thereof), and a polyhydric alcohol. These condensation products modified with an epoxy or amino compounds are also included in the term "unsaturated polyester resin". In general, they are used in a form of a mixture with a copolymerizable unsaturated monomer.

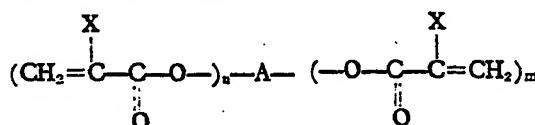
As the unsaturated polybasic acid (or anhydride thereof) there can be mentioned, for example, maleic acid, maleic anhydride, fumaric acid, citraconic acid, itaconic acid

and the like. As the saturated polybasic acid (or anhydride thereof) there can be exemplified phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, tetrachlorophthalic anhydride, hexachloroendomethylene tetrahydrophthalic acid, tetrabromophthalic anhydride, endomethylene - tetrahydrophthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, succinic acid, adipic acid, azelaic acid, sebacic acid, an anthracene - maleic anhydride adduct, a rosin - maleic anhydride adduct, trimellitic anhydride, pyromellitic anhydride, and methyl nadic acid.

As the polyhydric alcohol to be reacted with the above unsaturated polybasic component, there can be mentioned, for example, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, 1,4-butane diol, 1,3 - butane diol, 2,3 - butane diol, 1,5 - pentane diol, 1,6 - hexane diol, neopentyl glycol, 2,2,4 - trimethyl - 1,3 - pentane diol, hydrogenated bis - phenol A, 2,2' - bis(4 - hydroxyphenylene)propane, an adduct or reaction product between an alkylene oxide and 2,2' - bis(4 - hydroxyphenylene)propane, pentaerythritol, glycerin, trimethylene glycol, 2 - ethyl - 1,3 - hexane diol, phenyl glycidyl ether, allyl glycidyl ether, hexane triol, and sorbitol.

The copolymerizable unsaturated monomer preferably used in combination with the above unsaturated polyester resin is selected from vinyl, vinylidene, allyl and other compounds having at least one  $\alpha,\beta$  - ethylenical double bond in the molecule. Examples of such unsaturated monomer include styrene, vinyl-toluene, chlorostyrene,  $\alpha$  - methylstyrene, tert - butylstyrene, divinylbenzene, alkyl esters of methacrylic acid such as methyl methacrylate, alkyl esters of acrylic acid such as ethyl acrylate, vinyl acetate, acrylamide, methacrylamide, maleimide, diallyl phthalate, diallyl isophthalate, allyl acrylate, allyl methacrylate, diallyl maleate, diallyl itaconate, diallyl sebacate, diallyl adipate, diallyl glycolate and triallyl phosphate.

Compounds represented by the following general formula can also be used as the copolymerizable unsaturated monomer:



wherein A is a residue of a compound having at least two terminal hydroxy groups (e.g. a compound having at least one ester or ether linkage in the molecule and at least two terminal hydroxyl groups); X stands for hydrogen, halogen or an alkyl groups such as

methyl and ethyl; and n and m are integers of 1 to 3.

There may be exemplified ethyleneglycol dimethacrylate, propyleneglycol dimethacrylate, 1,3 - butanediol dimethacrylate, 1,4 - butanediol methacrylate, 2,3 - butanediol di-

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- methacrylate, 2 - ethyl - 1,3 - hexanediol dimethacrylate, 1,5 - pentanediol dimethacrylate, 1,6 - hexanediol dimethacrylate, neopentylglycol dimethacrylate, glycerin trimethacrylate, dimethacryl (bis - diethyleneglycol) phthalate, dimethacryl (bis - diethyleneglycol) maleate, tetramethacryl (bis - diethyleneglycol) phthalate, triethyleneglycol dimethacrylate, tetramethyleneglycol dimethacrylate, polyethyleneglycol dimethacrylate and trimethylolpropane trimethacrylate.
- These compounds have a boiling point higher than that of styrene and can be handled with ease. Further, even when they are added in very small amounts, the cross-linking density can be elevated and the heat distortion temperature can be heightened in the resulting cured molded article.
- As the copolymerizable unsaturated monomer, there can also be employed dialkyl esters of maleic acid, fumaric acid and itaconic acid, such as dimethyl maleate, diethyl maleate, dibutyl maleate, diethyl maleate, diethyl fumarate, diethyl itaconate and the like.
- These copolymerizable unsaturated monomers can be used singly or in the form of mixtures of two or more of them.
- In view of the water resistance and mechanical properties of the resulting molded article, it is preferable that the above-mentioned unsaturated polyester resin to be used in this invention have an acid value not exceeding 60, especially not exceeding 30, and a number average molecular weight of at least 200, especially at least 1000. It is also preferable that the mixing weight ratio of unsaturated polyester resin/copolymerizable unsaturated monomer be within a range of from 80/20 to 30/70, especially from 70/30 to 40/60.
- In order to lessen the shrinkage of the unsaturated polyester resin at the curing step, and improve the extrusion moldability of the resin and the surface smoothness and appearance of the resulting molded article, it is necessary that a thermoplastic resin be present in the extrudable composition, preferably dissolved in the above-mentioned copolymerizable unsaturated monomer. As such thermoplastic resin there can be mentioned, for example, copolymers of lower alkyl esters of acrylic or methacrylic acid, copolymers of methyl methacrylate with, for example, acrylamide, methacrylamide, acrylonitrile, styrene or the like, styrene - acrylonitrile copolymers, vinyl chloridevinyl acetate copolymers, saturated polyester resins, polyvinylacetate resins, polyamide resins, cellulose acetate butyrate resins, and the like. It is desirable that these thermoplastic resins have an average molecular weight of at least 10,000, especially of 25,000 to 500,000.
- The thermoplastic resin is preferably added in an amount of 1 to 20% by weight, more preferably 5 to 15% by weight, based on the sum of the unsaturated polyester resin and copolymerizable unsaturated monomer. In order to attain the low shrinkage and high heat resistance, it is desirable that the unsaturated polyester resin to be used comprises the unsaturated polybasic acid component in an amount of at least 50 mole %, especially of at least 75 mole %, based on the total acid components.
- A polymerization initiator is incorporated as a curing agent, preferably in an amount of 0.2 to 3% by weight based on the mixture of the above unsaturated polyester resin and copolymerizable unsaturated monomer.
- Organic peroxides of the high temperature decomposition type in which the decomposition temperature necessary for obtaining a half-value period of 1 minute is higher than 150°C are preferably used as the polymerization initiator in this invention. As such initiator, there may be exemplified methyl ethyl ketone (said decomposition temperature (abbreviated to "d.t." hereinbelow) being 171°C), cyclohexanone peroxide (d.t.=174°C), tert - butyl hydroperoxide (d.t.=179°C), p- (or m-)methane hydroperoxide (d.t.=216°C), cumene hydroperoxide (d.t.=255°C), 2,5 - dimethylhexane - 2,5 - dihydroperoxide (d.t.=257°C), tert - butyl perbenzoate (d.t.=170°C), tert - butyl peracetate (d.t.=160°C), di - tert - butyl peroxide (d.t.=186°C), dicumyl peroxide (d.t.=171°C), 2,5 - dimethyl - 2,5 - di(tert-butyl - peroxy)hexane (d.t.=179°C, 2,5 - dimethylhexane - 2,5 - di(hydroperoxide) (d.t.=257°C), diisopropyl benzene hydroperoxide (d.t.=205°C), di - tert - butyl perphthalate (d.t.=159°C), etc. These polymerization initiators may be used singly or in the form of admixtures of two or more of them.
- It is possible to employ a combination of an organic peroxide of the high decomposition temperature type such as mentioned above with a polymerization initiator of the low temperature decomposition type in which said decomposition temperature is not higher than 150°C. As such initiator of the low temperature decomposition type, there may be exemplified benzoyl peroxide (d.t.=130°C), p - chlorobenzoyl peroxide (d.t.=137°C), 2,4 - dichlorobenzoyl peroxide (d.t.=121°C), propionyl peroxide (d.t.=118°C), lauroyl peroxide (d.t.=114°C), acetyl peroxide (d.t.=123°C), tert - butylperoxy isobutyrate (d.t.=133°C), succinic acid peroxide (d.t.=131°C), di - isopropylperoxy dicarbonate (d.t.=38°C),  $\alpha,\alpha'$  - azobisisobutyronitrile (d.t.=106°C), etc. It is preferred that such polymerization initiator of the low temperature decomposition type is used in an amount of up to 20% by weight based on the total amount of polymerization initiators used.
- It is also possible to add a curing promotor

such as Co, Mn and Fe salts of organic acids, dimethylaniline, diethylaniline and the like.

It is especially preferable that the unsaturated polyester resin used in this invention have a high hot strength or its molded article have a Rockwell hardness of at least 100 (R scale) at room temperature.

As the thermosetting phenol resins to be used in this invention, there can be mentioned so-called resol type resins obtained by reacting phenol, cresol, xylenol or the like with an excess of formaldehyde, p - formaldehyde, acetaldehyde or the like, and novolak type resins obtained by reacting an aldehyde such as mentioned above with an excess of a phenol such as mentioned above. The former resins are cured by heating or by addition of an acid at room temperature, and the latter resins are cured by adding p - formaldehyde, hexamethylene tetramine or the like and a divalent metal oxide as a promotor and heating the mixture.

It is possible to use a butadiene - styrene copolymer, a butadiene - acrylonitrile copolymer or a similar synthetic rubber as a modifier for the above-mentioned phenol resin.

The thermosetting epoxy resin used in this invention is a macromolecular compound which comes finally to have a three-dimensional structure as a result of the reaction between an organic compound having at least two epoxide groups in the molecule and a curing agent. As such thermosetting epoxy resin there can be mentioned, for example, glycidyl ether type epoxy resins such as bisphenol A type epoxy resins, resorcin type epoxy resin, bis - phenol F type epoxy resins, tetrahydroxyphenyl ethane type epoxy resins, novolak type epoxy resins and polyglycol type epoxy resins; glycidyl ester type epoxy resins; methyl-substituted epoxy resins; alicyclic epoxy resins; polyolefin type epoxy resins; glycidylamine type epoxy resins; halogenated epoxy resins; and epoxidized soybean oil. These epoxy resins can be used singly or in the form of mixtures of two or more of them.

As the curing agent for such epoxy resin, there can be mentioned, for example, polyamines such as aliphatic polyamines, aromatic polyamines and alicyclic polyamines; tertiary amines;  $\text{BF}_3$  complex compounds; imidazoles, imidazolines; organic acid anhydrides such as phthalic anhydride, maleic anhydride and trimellitic anhydride; and other curing agents such as dicyandiamide, diacid hydrazide, amine adducts of epoxy resins, amine adducts of ethylene oxide or propylene oxide, and morpholine. Still in addition, urea-formaldehyde resins, melamine - formaldehyde resins, phenol - formaldehyde resins, aniline-formaldehyde resins, polyhydric phenols and polyvalent isocyanates can be suitably used as the curing agent for the epoxy resin. It is also possible to employ the epoxy resin in the state admixed with a reactive diluent

such as octylene oxide, styrene oxide, butyl glycidyl ether, cyclohexene vinyl monoxide, and acryl glycidyl ether.

The polyurethane resin used in this invention is a macromolecular compound that can be obtained by reacting a polyisocyanate compound having at least 2 isocyanate groups in the molecule and a compound having at least two active hydrogen atoms in the molecule.

As the polyisocyanate compound, there can be mentioned, for example, ethylene diisocyanate, hexamethylene diisocyanate, decamethylene diisocyanate, phenylene diisocyanate, tolylene diisocyanate, naphthylene diisocyanate, 4,4' - methylene - bis(phenylisocyanate), 4,4' - ethylene - bis(phenylisocyanate), 3,3' - diisocyanate - 1,4 - dimethylbenzene, 1 - methyl - 2,4 - diisocyanate - cyclohexanone, 3,3' - diisocyanate - diethylbenzene, 3,3' - diisocyanate - dimethyltoluene, 3,3' - diisocyanate - dimethyl - xylene, 3,3' - diisocyanate - diethylxylene, 4,4' - methylene - bis(cyclohexylisocyanate), 4,4' - ethylene - bis(cyclohexylisocyanate), isophoronediamine diisocyanate, lysine isocyanate and triphenylmethane isocyanate. It is possible to employ a mixture of an excess of such polyisocyanate with a low-molecular-weight polyol as a component causing addition reaction and chain extension, such as ethylene glycol, propylene glycol, 1,3-butylene glycol, neopentyl glycol, 2,2,4 - trimethyl - 1,3 - pentane diol, hexamethylene glycol, cyclohexane dimethanol, trimethanol propane, hexane triol, glycerin, sorbitol, sucrose and pentaerythritol. It is also possible to employ these polyisocyanate compounds in such state that their isocyanate groups are temporarily masked with a blocking agent of the phenol, lactam, active methylene, alcohol, mercaptan, acid amide, imide, amine, imidazole, urea, carbamate, imine, oxime or sulfite type.

As the active hydrogen-containing compound, there are employed polyhydroxy compounds, polycarboxylic compounds and polyhydroxycarboxylic compounds. Typical instances of the active hydrogen-containing compound include polyester polyols having a molecular weight of 200 to 5000, polyether polyols having a molecular weight of 2000 to 6000, castor oil derivatives, tall oil derivatives, and polybutadienes having hydroxy groups at both the terminal ends of the molecule.

In the case of the polyurethane resin, a foamed article can be easily obtained by reacting the above-mentioned polyol and polyisocyanate with water or a blowing agent.

The allyl resin used in this invention is a diallyl ether formed by condensation reaction between a polybasic acid and allyl alcohol, or a prepolymer thereof. An organic

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|    | peroxide is incorporated in such allyl resin to cause the curing reaction.   | 65                    |     |
| 5  | If desired, the composition to be extruded may contain a mold-release agent such as stearic acid and aluminium stearate; a thickener such as a finely divided silica and bentonite; a dispersing agent such as an anionic, cationic or non-ionic surfactant; a lubricant such as paraffin wax, chlorinated paraffin, and fluorocarbon; a blowing agent of the nitroso, sulphonydrazide, azo or inorganic type; a blowing assistant of the urea, organic acid or metal salt type; a flame retardant such as tricresyl phosphate, triphenyl phosphate and antimony oxide; a colorant such as a dye or a pigment; a curing promoter; a polymerization inhibitor; an antioxidant; an antistatic agent; or a stabilizer.  | 70                    |     |
| 10 | The filler present in the composition can be, for example, magnesium carbonate, silica, clay or talc. The fibrous material present in the composition can be, for example, glass fibres, steel fibres, organic fibres, asbestos fibres or carbon fibres.   | 75                    |     |
| 15 | As a thermosetting resin is present in the composition used in this invention, the flow characteristics and moldability of the resin are improved, with the result that the appearance, toughness, impact resistance and other properties are improved in the resulting molded article. The thermoplastic resins are preferably used in the form of powders having a particle size not exceeding 100 $\mu$ , preferably not exceeding 20 $\mu$ . Examples of suitable thermoplastic resins are polyethylene, polypropylene, polybutene, polyvinyl chloride, polyvinyl formal, polyvinyl butyral, polyvinylidene chloride, polymethacrylate, polyamide, polycarbonate, polyvinyl fluoride, polyvinylidene fluoride, and acetyl cellulose.   | 80                    |     |
| 20 | The thermoplastic resin is present in an amount of up to 50% by weight based on the total resin components.  | 85                    |     |
| 25 | Especially when a powder of polyethylene or polyvinyl chloride is incorporated in an unsaturated polyester resin, the shrinkage is extremely reduced at the curing step and the finished appearance of the molded article can be highly improved.  | 90                    |     |
| 30 | This invention will now be illustrated by reference to the following Examples, in which "parts" and "%" are on a weight basis unless otherwise indicated. The abbreviation "DOP" used in the Examples means "di-octyl phthalate".  | 95                    |     |
| 35 | Example 1<br>25 parts of an unsaturated polyester resin solution (isophthalic acid/maleic anhydride/propylene glycol/neopentyl glycol in a mole ratio of 1:1:1.1:1.1, acid value=18, number average molecular weight=2200, styrene content=30%) in which 2% of a lauroyl peroxide paste (LPO/DOP=1:1) had been dissolved in advance, 14 parts of a powdery polyvinyl chloride resin, 55 parts of barium sulfate, 1 part of a liquid composite stabilizer (Zn-Cd-Ba liquid organic complex), 5 parts of asbestos fibres and 1 part of stearic acid were roughly kneaded by a kneader and fed to an extruder to perform kneading. Extrusion molding was conducted by extrusion first through a preliminary die and then through an open-ended die passage, to give a hollow cylindrical extrudate having an outer diameter of 60 mm and a thickness of 3 mm. Cooling was conducted so that the interior of the cylinder of the extruder was maintained below 50°C, and the temperature of the extrudate from the preliminary die was controlled to 60±1°C by heating the preliminary die. Continuous and uniform extrusion was possible. The viscosity of the extrudate from the preliminary die corresponded to a needle penetration degree of 280. | 65                    |     |
| 40 | The temperature of the die passage was maintained at 150°C and the molding pressure was about 15 kg/cm <sup>2</sup> . The molding was accomplished for a residence time of 1 minute and a continuous pipe-like molded article was obtained. When water heated at 100°C was passed through the so obtained pipe, defects such as distortion or leakage were not observed.   | 70                    |     |
| 45 | Example 2<br>Extrusion molding was conducted using the same extruder, preliminary die and open-ended die passage as employed in Example 1. An unsaturated polyester resin solution as used in Example 1 in which 2% of a lauroyl peroxide paste (LPO/DOP=1:1) had been uniformly dissolved, a powdery polyvinyl chloride resin, calcium carbonate, stearic acid and organic synthetic fibres (having a length of 10 mm) were fed continuously to the extruder so that the resulting composition had a composition of 25 parts of the unsaturated polyester resin solution, 5 parts of the powdery polyvinyl chloride resin, 65 parts of calcium carbonate, 1 part of stearic acid and 5 parts of the organic synthetic fibres. Molding conditions adopted for continuous operation of the extrusion molding machine are shown in the Table below.  | 75                    |     |
| 50 | The resulting pipe-like molded article was excellent in surface finish and had excellent physical properties.  | 100                   |     |
| 55 | TABLE  | 105                   |     |
| 60 | Inlet temperature of cylinder of extruder  | 40°C                  | 110 |
|    | Outlet temperature of cylinder of extruder   | 60°C                  | 115 |
|    | Outlet temperature of preliminary die  | 68°C                  |     |
|    | Temperature of die passage   | 130°C                 | 125 |
|    | Molding pressure in die passage  | 15 kg/cm <sup>2</sup> |     |
|    | Residence time in die passage  | 1 minute              |     |

## WHAT WE CLAIM IS:—

1. A method of forming a molded and cured product, which comprises (1) continuously extruding from an extruder through a preliminary die either into an open-ended die passage or into the space between opposed endless moving belts, an extrudable composition comprising (a) a thermosetting resin selected from unsaturated polyester resins, epoxy resins, phenolic resins, urethane resins and allyl resins, (b) a thermoplastic resin in an amount of up to 50% by weight based upon the total weight of thermoplastic resin and thermosetting resin, (c) a filler, (d) a fibrous material and (e) a curing agent, such that the extrudate from the preliminary die has a flowability corresponding to a "needle penetration degree", as defined herein, of at least 20 and such that the composition does not completely cure in the extruder or preliminary die; and (2) curing the extrudate from the preliminary die in the open-ended die passage or in the space between the opposed endless moving belts, the curing being effected at a pressure not greater than 200 kg/cm<sup>2</sup>, the average temperature of the extrudate in the die passage or in the space between the belts being from 80 to 250°C, and the residence time of the extrudate in the die passage or in the space between the belts being from 1 second to 5 minutes.
2. A method according to Claim 1, wherein kneading and extrusion of the extrudable composition are effected simultaneously.
3. A method according to Claim 1 or 2, wherein the extrudable composition is extruded while heating it in the extruder at a temperature not exceeding the curing temperature of the thermosetting resin.
4. A method according to any one of the preceding Claims, wherein the thermosetting resin is an unsaturated polyester resin, and wherein the extrudable composition contains a copolymerizable unsaturated monomer.
5. A method according to any one of the preceding Claims, wherein the extrudable composition additionally contains a mold-release agent, a thickener, a dispersing agent, a lubricant, a blowing agent, a blowing assistant, a flame retardant, a colorant, a curing promoter, a polymerization initiator, an antioxidant, an antistatic agent or a stabilizer.
6. A method according to any of the preceding Claims, wherein extrusion is carried out in a screw-type extruder.
7. A method according to Claim 6, wherein extrusion is carried out using an extruder substantially as hereinbefore described with reference to, and as shown in, Figure 2 or Figure 2 as modified by any one of Figures 3 to 5 of the accompanying drawings.
8. A method in accordance with Claim 1 of forming a molded and cured product, substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.
9. A molded and cured product whenever formed by the method claimed in any of the preceding Claims.

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1453 516

4 SHEETS

COMPLETE SPECIFICATION

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SHEET 1

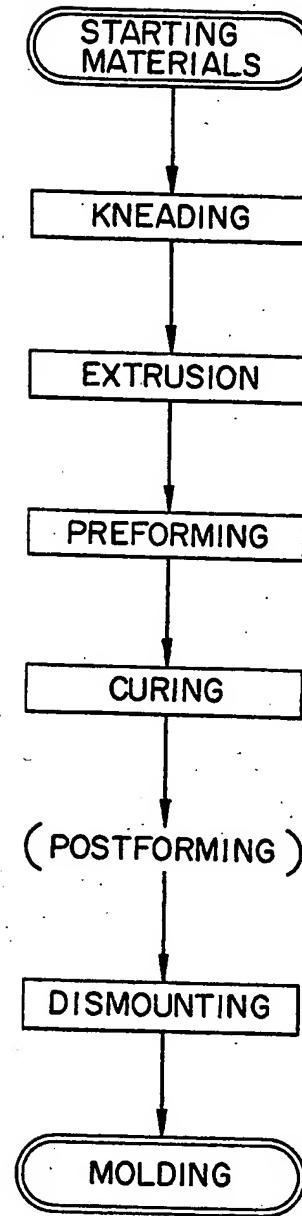


FIG. I

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SHEET 2

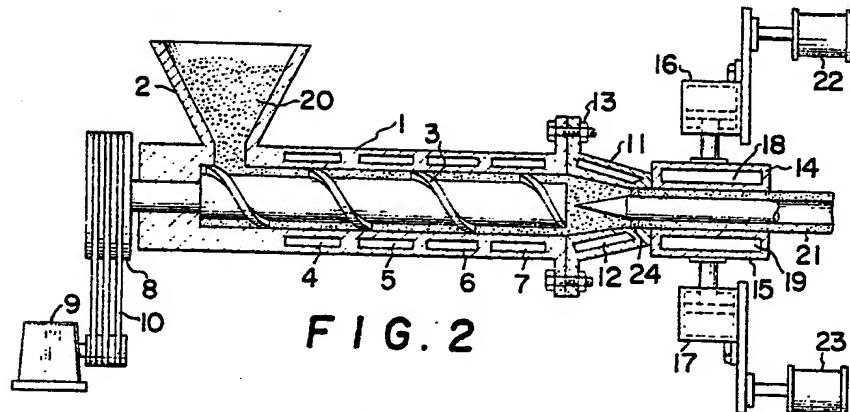


FIG. 2

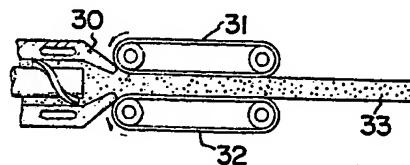


FIG. 3

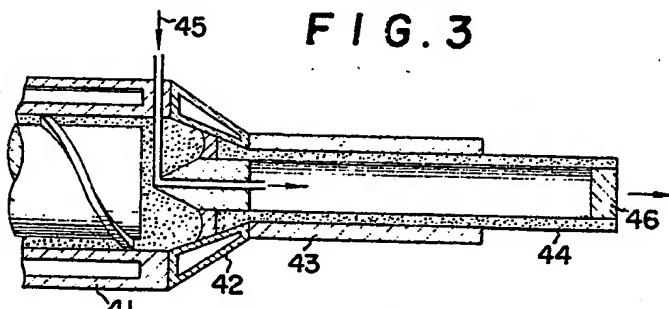


FIG. 4

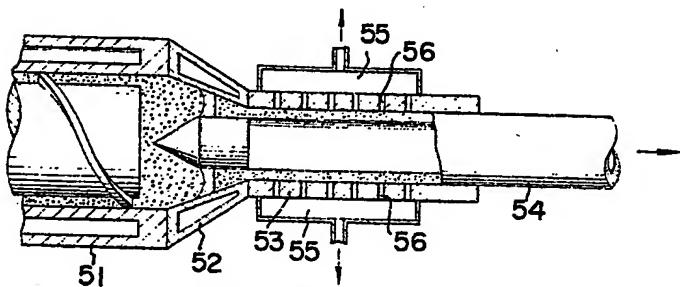
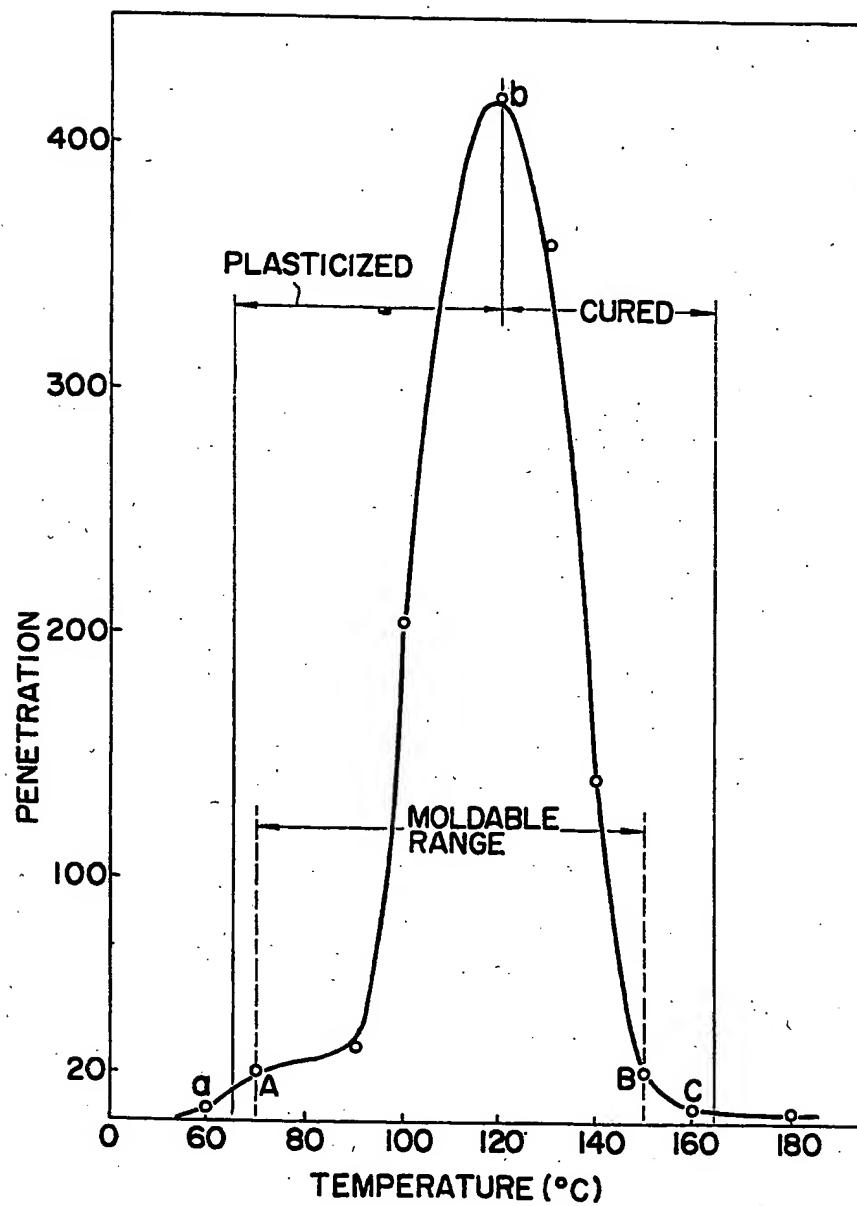


FIG. 5

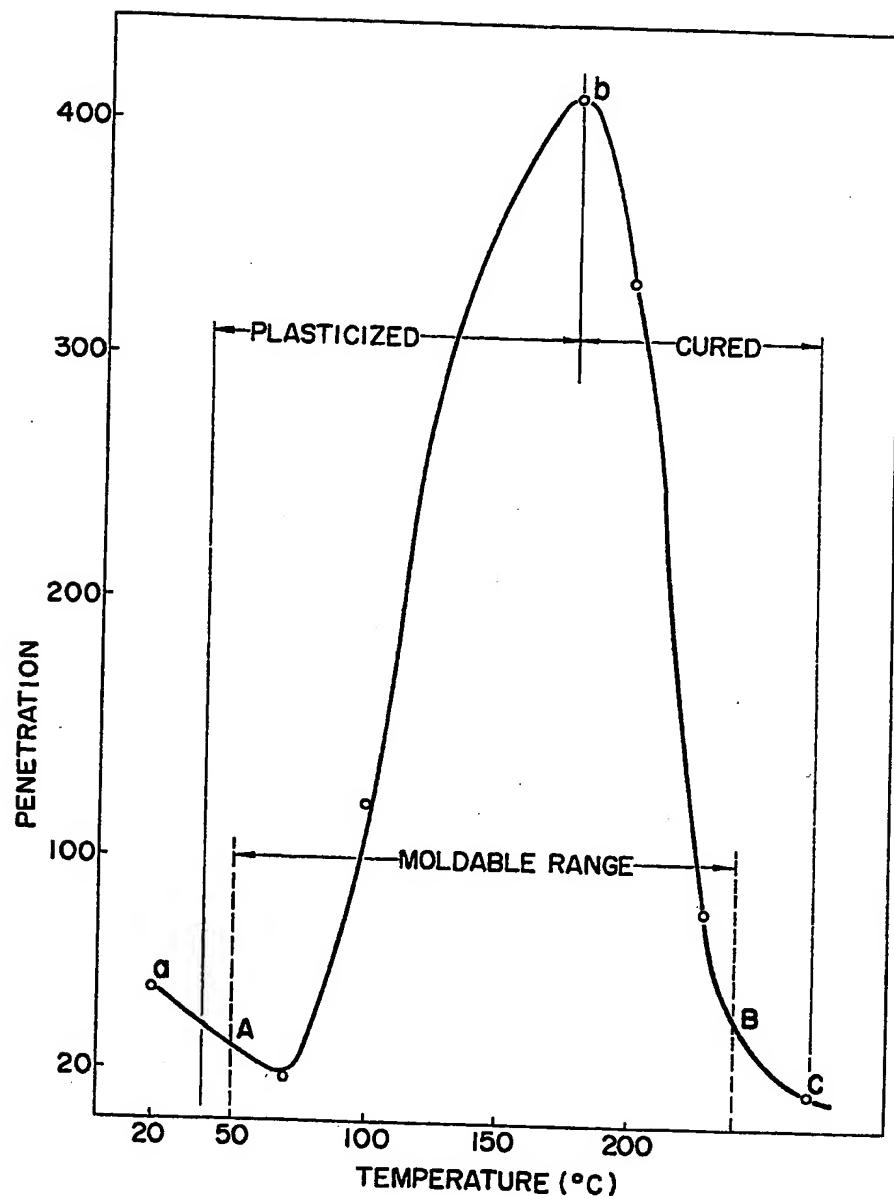
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SHEET 3



F I G. 6



F I G . 7